GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION
SPONSORED PROJECT INITIATION

Date: 10/21/80

Project Title: Cation Effects in Organoalkali Metal Chemistry; Organocesium Chemistry

Project No: G-33-670

Project Director: E. Grovenstein

Sponsor: National Science Foundation; Washington, D. C.

Agreement Period: From 9/1/80 Until 2/28/82
(Grant Period includes 6 month unfunded flexibility period)

Type Agreement: Grant No. CHE-8009810

Amount: $60,000 NSF*
10,762 GIT (G-33-328)
$70,762 TOTAL

Reports Required: Progress Report containing request for continued support; Final Report

Sponsor Contact Person (s):

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(thru OCA)

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*This is a continuing grant which has been approved for approximately 3 yrs. Contingei on availability of funds and scientific progress, NSF expects to continue support at $60,000 for FY81 and $60,000 for FY82.

Defense Priority Rating: None

Assigned to: Chemistry (School/~~Laboratory~~)

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N-T-IF 8 - JR 306

GEORGIA INSTITUTE OF TECHNOLOGY OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT TERMINATION/CLOSEOUT SHEET

Date 10/12/83

Project No. G-33-670 School ~~xxx~~ Chemistry

Includes Subproject No.(s) NONE

Project Director(s) Dr. Erling Grovenstein GTRI ~~xxx~~

Sponsor National Science Foundation

Title: Cation Effects in Organoalkali Metal Chemistry: Organocesium Chemistry

Effective Completion Date: 2/28/82 (Performance) _____ (Reports)

Grant/Contract Closeout Actions Remaining:

- [X] None
- [ ] Final Invoice or Final Fiscal Report
- [ ] Closing Documents
- [ ] Final Report of Inventions
- [ ] Govt. Property Inventory & Related Certificate
- [ ] Classified Material Certificate
- [ ] Other _____

Continues Project No. _____

Continued by Project No. G-33-614

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Form OCA 58.1004

G-33-670

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

CHEMISTRY

July 21, 1981

TO: Dr. Kenneth G. Hancock
Program Director for Chemical Dynamics Program
National Science Foundation
Washington, D. C. 20550

FROM: Dr. Erling Grovenstein, Jr.
Principal Investigator
School of Chemistry
Georgia Institute of Technology
Atlanta, Georgia 30332

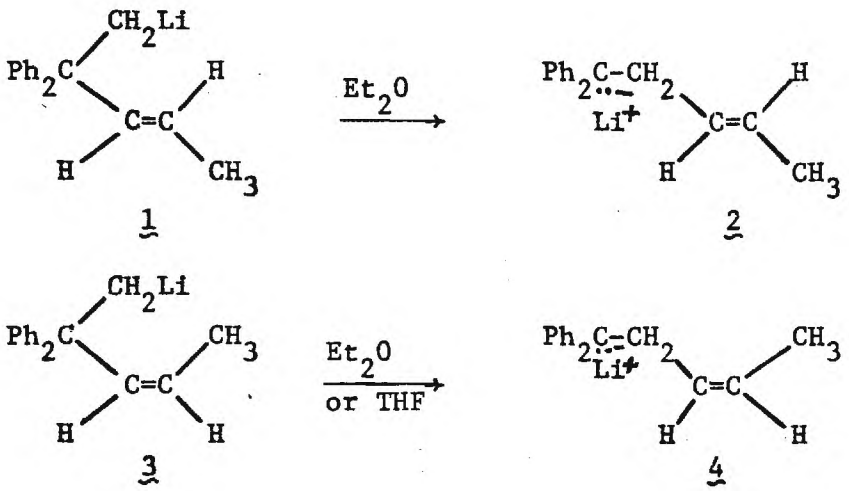
SUBJECT: Brief Technical Report upon "Cation Effects in Organoalkali Metal Chemistry; Organocesium Chemistry."
NSF Grant No. CHE-8009810
For Period December 1, 1980 - August 20, 1981.

First it should be noted for the present new grant that, while the award was effective as of September 1, 1980, because of the time required to find suitable personnel, work upon the new grant could not begin until December, 1980. Information to this effect was conveyed to NSF via a telephone conversation with Dr. Hancock (January 16, 1981) and it was agreed to extend the first year's program by three months.

Reprints of the following article on work completed under the prior NSF grant were mailed to the Foundation on October 10, 1980:

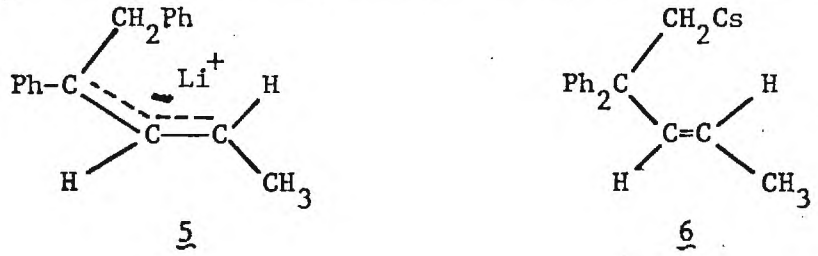
"Carbanions 20. Rearrangements in Reaction of 5-Chloro-4,4-diphenyl-2-pentyne, 1-Chloro-5,5-dimethyl-2,2-diphenyl-3-hexyne, and 5,5-Dimethyl-2,3-diphenyl-3-hexyne with Alkali Metals, Cation Effects on Migratory Aptitudes of Groups," Erling Grovenstein, Jr., Kuen-Wai Chiu, and Bhalchandra B. Patil, J. Amer. Chem. Soc., 1980, 102, pp 5848-5859.

The M.S. thesis of John H. Northrop on "The Rearrangement of trans-2,2-diphenyl-3-pentenyllithium" was completed June, 1981. Captain Northrop's work was partially supported by the present grant (chemicals and supplies); the remainder of his support was from the United States Military Academy, West Point, New York, which sent Captain Northrop to the Georgia Institute of Technology for advance training in Chemistry. In conjunction with the prior work in our laboratories of D. L. Streeter, Northrop finds that both cis- and trans-2,2-diphenyl-3-pentenyllithium (1 and 3) (formed from reaction of the corresponding chlorides with lithium in diethyl ether at -78°C) in Et_2O at 35°C undergo [1,2] migration of the propenyl group with essentially complete retention (98 $\pm$ 2%) of stereochemistry:



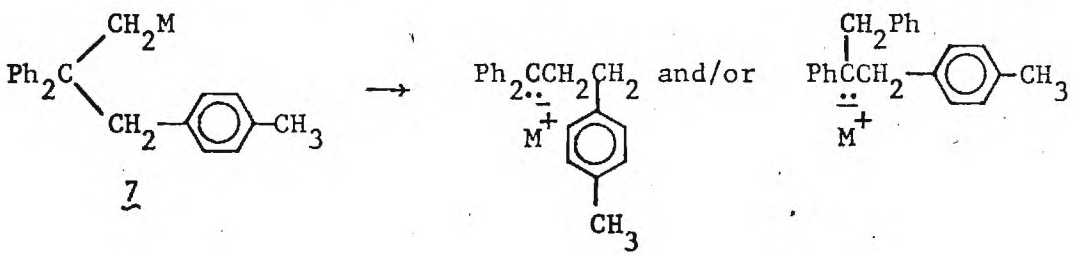
.so in THF the trans isomer undergoes propenyl migration with 98 ± 2% retention of onfiguration of the migrating group. These results are of theoretical and practical iterest, in part because A. Maercker and W. Streit [Angew. Chem. Int. Ed., 1972, 11, 542-543] and E. A. Hill [J. Organomet. Chem., 1975, 91, pp 123-271] have observed iat [1,2] migration of the propenyl group in Grignard reagents is NOT stereospecific. ie present is an example of a cation effect in organometallic chemistry: the properties f "carbanions" are modified by the nature of the cation to which they are attached and y the ligands which lie within the coordination sphere of the cation.

When the solvent is changed from Et_2O to THF, the trans-organolithium compound 1 on warming to 10°C gives only 39% of 2, the product of vinyl migration, and mainly ives 5, the product of [1,2] phenyl migration. In Et_2O at 35°C, in contrast, the ratio f 2 to 5 is 97 to 3. The rearrangement of the corresponding organocesium compound 6 has

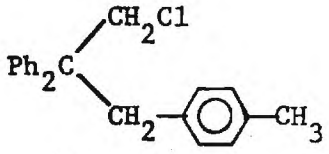


een studied; however, product analysis is not yet complete.

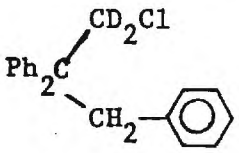
Randall L. Hughes (who receives partial support from the present grant) began in the ring a study of cation and solvent effects upon the relative migratory aptitudes of -methylbenzyl and phenyl groups in 7. At the present time synthesis of the precursor



f 7, namely the chloride 8, is complete and synthesis of 9 is underway with aid of



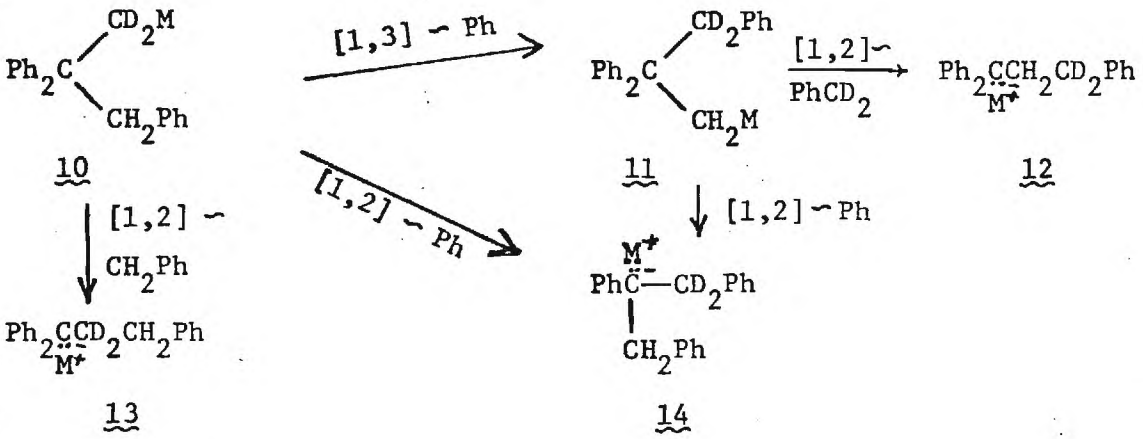
8



9

iss Karla Walker (NSF Summer Research Participant). Compound 9 is desired as a recursor of 10. With compound 10 (see Scheme I) we should be able to discover if [1,3]

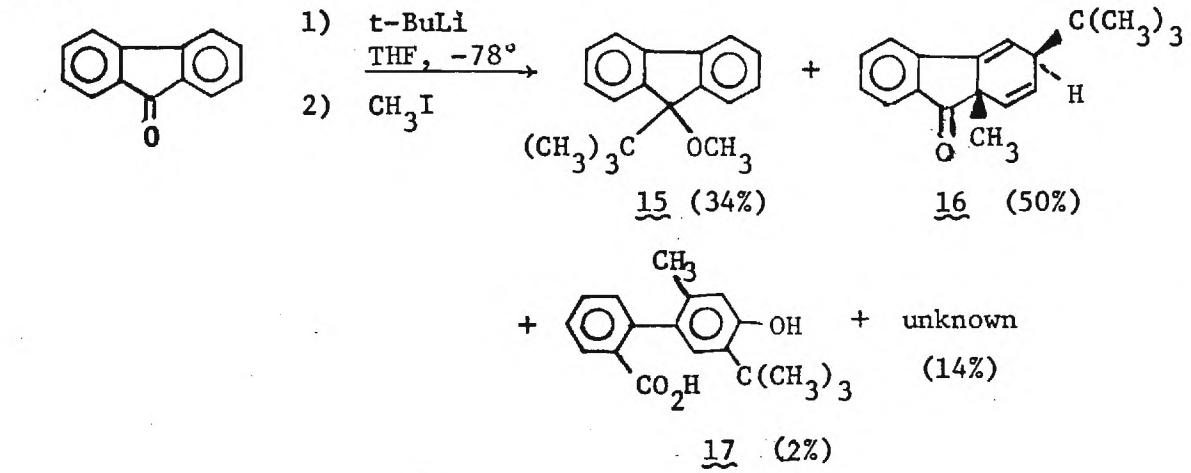
cheme I



igration of phenyl is competitive with [1,2] migration of phenyl and benzyl. There is n implication in some of our earlier work that [1,3] migration of aryl occurs more eadily than [1,2] but this has never been definitively tested. Such a result would be urprising since in both carbonium ion and free radical rearrangements [1,2] migrations re more facile than [1,3] migrations. [cf M. Saunders, J. Chandrasekhar, and P.v.R. chleyer in "Rearrangements in Ground and Excited States," P. deMayo, ed., Academic ress, N.Y., Vol. 1, (1980), pp 1-48; J. W. Wilt, "Free Radicals," J. K. Kochi, ed., ohn Wiley & Sons, N.Y., Vol. 1, (1973), p 333-501].

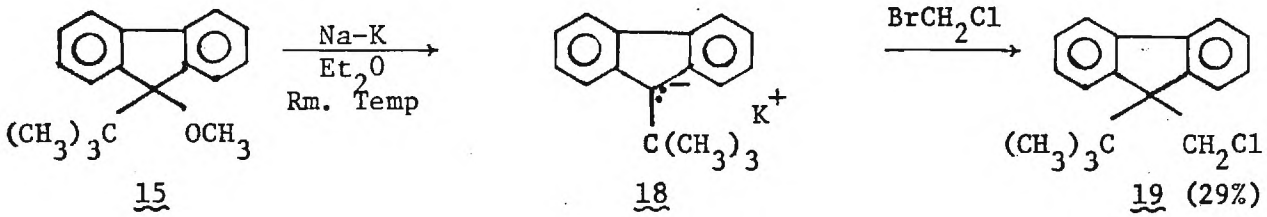
In another area Dr. J. Singh has synthesized 9-chloromethyl-9-tert-butylfluorene (19) y the process outlined in Scheme II. This synthesis proved much more difficult than nticipated. The desired methyl ether 15 was one of only several products formed. The tructures of the compounds 16 and 17 were determined by single crystal x-ray diffraction. n improved yield of intermediate 15 can be obtained by carrying out the addition of -butyllithium to fluorenone in benzene or toluene as solvent, followed by protonation, solation of the alcohol, and then methylation. Evidently there is much steric compression

heme II



15 (34%) 16 (50%)

17 (2%)

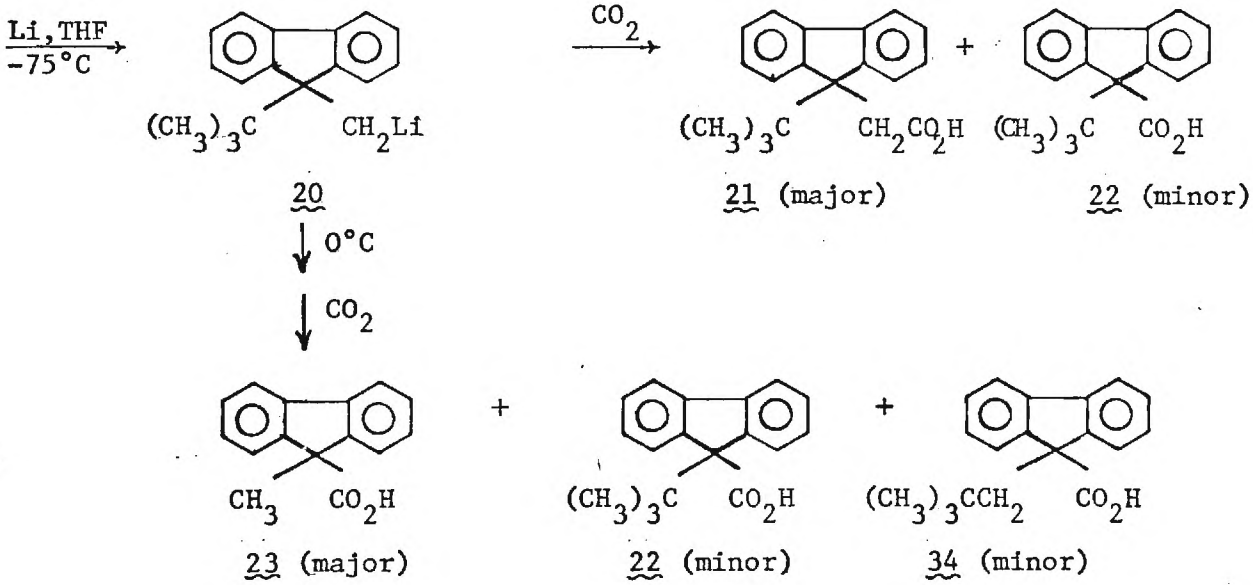


15 18 19 (29%)

15 and in the chloride 19 such as to make syntheses in this area difficult and the mpounds fragile (the methyl ether 15 decomposed during attempted recrystallization from iling hexane). The origin of compound 17 is obscure; evidently it arose from oxidation ring work-up of a labile intermediate — 15 and 16 are not readily oxidized by air. anks to the skill and patience of my collaborator, Dr. Singh, we have perservered in is area with some interesting results.

Reaction of the chloride 19 with lithium in THF gave the results outlined in Scheme III.

heme III



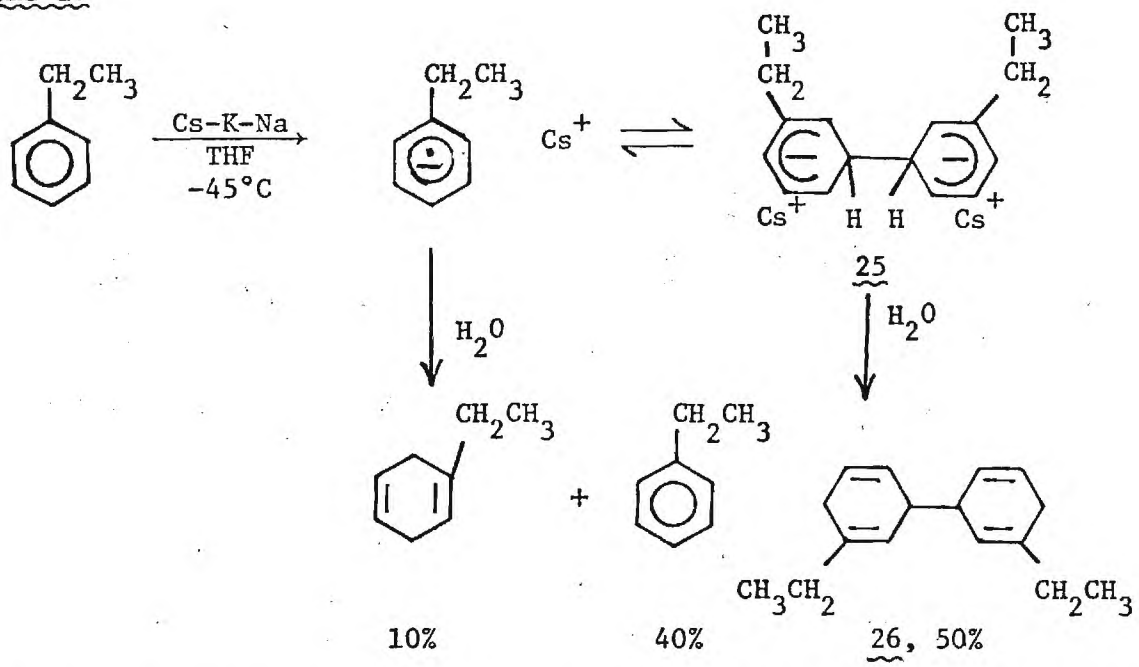
20 21 (major) 22 (minor)

23 (major) 22 (minor) 34 (minor)

Singh's work with chloride 19 confirms the major results of B. B. Patil in our laboratory who had made the organolithium compound 20 by a new untested route. The origin of the minor acid 22 may be from 9-t-butylfluorene in the chloride 19; however, the quantity of 22 seems too large for this route. The origin of the neopentyl compound 24 is even more obscure; it appears to result from a [1,2] migration of the t-butyl group of 20. This would be an unprecedented result for rearrangement of an organolithium compound containing only carbon and hydrogen but tert-alkyl migrations are known in Wittig ether rearrangements and are thought to occur by fragmentation into radical pairs [cf. P. T. Lansbury, et al., J. Amer. Chem. Soc., 1966, 88, p. 78; V. Schöllkopf, Angew. Chem. Int. Ed. Eng., 1970, 9, p 763].

Dr. A. M. Bhatti has continued our study of reaction of cesium and Cs-K-Na alloy with hydrocarbons and other simple compounds. He finds that the following reactions occur as deduced by protonation of the intermediate organocesium compounds (see Scheme IV).

Scheme IV

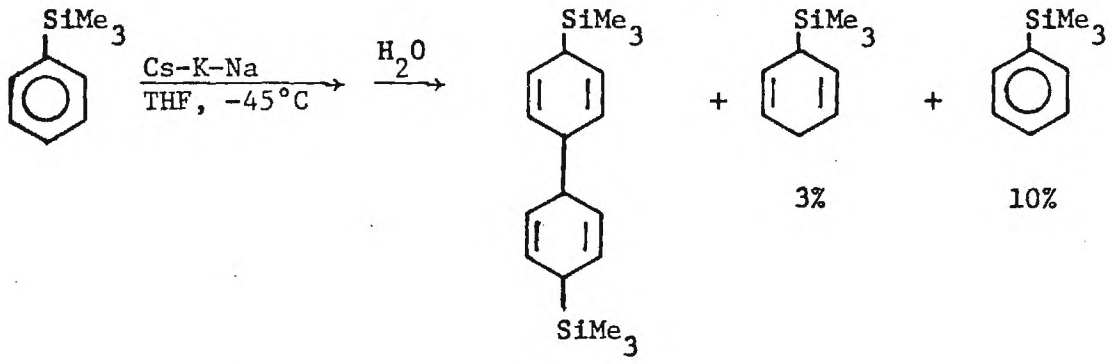


With ethylbenzene a reasonably good yield of the dimer 26 (new compound) is obtained. An outstanding result here is the high regiospecificity in dimerization of the radical anion of ethylbenzene. The structure of 26 was deduced via its analytical and spectroscopic properties and especially by dehydrogenation by DDQ to m,m'-diethylbiphenyl. All six of the possible diethylbiphenyls were prepared having one ethyl group on each phenyl group. A careful GC analysis of the product of dehydrogenation of 26 failed to detect any of these isomers in the sample of 26.

It was shown that the GC method could detect less than 0.3% of each of these isomers and thus the dehydrogenation product is > 98.8% pure 3,3'-diethylbiphenyl.

An attempt to carry out a similar reaction of Cs-K-Na alloy with isopropylbenzene failed to produce detectable dimer and gave only about 1% of dihydroisopropylbenzene. It is planned to repeat this reaction at -78°C to see if more extensive reaction can be observed.

Whereas tert-butylbenzene similarly fails to undergo appreciable reaction with Cs-K-Na alloy in THF (unpublished earlier work with D. E. Quest), the related compound trimethylsilylbenzene reacts in good yield:



27, 82%

In this case, the product 27 appears to be exclusively p,p'-bis(trimethylsilyl)-biphenyl according to GC analysis of its product of dehydrogenation by DDQ. No evidence of structural isomers of 27 exist by GC and NMR analysis of the dehydrogenation product; however, the 300 MHz ^{1}H NMR of 27 suggests that three stereochemical isomers of 27 are formed (cis,cis-; trans,trans-; and cis,trans-isomers). Thus while dimerization of the radical anion of trimethylsilylbenzene is regiospecific as is also protonation of the dimer, protonation of the dimer is not stereospecific.